

# REACTOR MODELING AND PHYSICAL-CHEMICAL PROPERTIES CHARACTERIZATION IN POLYETHYLENE FLUIDIZED-BED REACTOR

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## INTRODUCTION

Although the fluidized-bed reactor technology for producing polyethylene has been invented on the 50s, and its commercial use has been growing since the last decade, little is still known about its behavior regarding to temperature, concentration, production and polyethylene physical-chemical properties characterization gradients inside the reactor.

In the past years, some researchers have focused their attention to the modeling of these polyethylene gas-phase processes (Choi & Ray, 1985; McAuley et al., 1994) but, even though, these models are based on strong assumptions such as a well-mixed emulsion phase, which can be easily brought down when considering low degree or no pre-polymerization. In the latter cases, heat and mass transfer resistances become significant and the polymerization rate of young particles can lead to over-heating.

In order to create a more reliable model for the fluidized-bed reactor, a steady-state model incorporating interactions between separate bubble and emulsion phases inside the reactor bed has been developed. A polymer physical-chemical characterization model has also been developed and the linkage of these two models has been studied.

## MODEL DEVELOPMENT

The assumptions that have been made in the development of the model are summarized below.

- The fluidized bed comprises two phases: bubble and emulsion phases.
- The polymerization reactions occur only in the emulsion phase.
- The emulsion phase is at minimum fluidizing conditions.
- The emulsion phase is not well-mixed.
- The gas in excess of that required for maintaining the minimum fluidizing condition passes through the bed as bubble phase.
- The bubbles are spherical and of uniform size throughout the bed, reaching a maximum stable size. The bubbles travel up through the bed at a constant velocity in a plug-flow regime.
- There are a negligible radial gradient of temperature and concentration in the bed, due to the agitation produced by the up flowing gas.
- There is negligible resistance of heat and mass transfer between gas and solids in the emulsion phase.
- There is no agglomeration between polymer particles throughout the bed.
- Elutriation of fines from the bed are not considered.
- The polymer particle grows and segregates inside the reactor.
- The gas-phase is composed by ethylene, 1-butene, 1-hexene, nitrogen and hydrogen

All mass and energy balances were given in the differential form, in order to account for gas concentrations (ethylene, 1-butene, 1-hexene, hydrogen and nitrogen) and temperature axial gradients along the reactor in both phases. This means that the reagent gases are in a plug-flow regime but at different velocities for bubble and emulsion phases.

*Bubble-phase material and energy balances*

$$\frac{dC_{bi}}{dz} = \frac{K_{mi}}{U_b} \cdot (C_{ei} - C_{bi})$$
$$\frac{dT_b}{dz} = \frac{H_m}{U_b \cdot C_{bT} \cdot c_{pgT}} \cdot (T_b - T_e)$$

#### Emulsion-phase material and energy balances

$$\frac{dC_{ei}}{dz} = \frac{Rp' \cdot (1 - \varepsilon_{mf})}{\varepsilon_{mf} \cdot A \cdot U_e} + \frac{K_{mi} \cdot (C_{bi} - C_{ei}) \cdot \delta}{(1 - \delta) \cdot \varepsilon_{mf} \cdot U_e}$$

$$\frac{dT_e}{dz} = \frac{\left[ \sum_{i=1}^{NC} \dot{c}_{pgi} \cdot K_{mi} \cdot (C_{bi} - C_{ei}) + Hm \right] \cdot (T_b - T_e) \cdot \delta}{U_e \cdot (1 - \delta) \cdot \varepsilon_{mf} \cdot \dot{c}_{pgT} \cdot C_{eT}}$$

$$\frac{Rp' \cdot (1 - \varepsilon_{mf}) \cdot M_w \cdot \left[ -\Delta H - (c_{ps} - c_{pgT}) \cdot (T_e - T_{ref}) \right] + \pi \cdot D \cdot U_h \cdot (T_e - T_\infty)}{U_e \cdot \varepsilon_{mf} \cdot \dot{c}_{pgT} \cdot C_{eT}}$$

The new approach given by this study relies on the average weight fraction of catalyst in the polymer, which is not constant along the reactor and has been equated also in a differential form depending mainly on the polyethylene production. In this way it is possible to simulate that there is a high catalyst/polymer mass weight fraction at the top of the reactor and a low mass weight fraction at the base, what is in accordance with the fact that there exists a degree of segregation of the different polyethylene particle sizes in the fluidized-bed reactor.

#### Average mass weight fraction of catalyst in the polyethylene

$$\frac{d\chi}{dz} = \frac{Rp' \cdot A \cdot (1 - \delta) \cdot (1 - \varepsilon_{mf}) \cdot M_w}{\chi \cdot q_{cat}}$$

The great advantage in having this new variable is that it allows the usage of a more complex reaction mechanism, which is summarized in Table 1. Not only that but it gives strong support to predict the growth of polyethylene particles along the fluidized-bed.

It is important to state that the mathematical resolution of the model followed the physical design of the reactor, where the gas and polymer particles flow in countercurrent, the gas is fed at the base and the catalyst at the top portion of the reactor. This design configuration implies on having contour conditions at the base and top of the reactor, what resulted in an iterative resolution of the system till all base and top contour conditions were satisfied. The final reactor model was composed of 10 differential equations, plus accessories equations for the calculation of the particle growth throughout the reactor.

The reaction mechanism used in this work is the same described by Kissin (1987), de Carvalho et al (1989) and McAuley et al (1990). In general, this mechanism is based upon the coordination copolymerization of ethylene using Ziegler-Natta catalyst with two different types of catalyst sites. Each site type is associated with different rate constants for formation, initiation, propagation and chain transfer. Only the effects of the terminal monomers were considered on the reaction rates.

Alongside to the reactor model, the method of moments (Zabisky et al, 1992) has been used to create a new mathematical model capable of predicting the physical-chemical characteristics of the polyethylene (average molecular weight, density, polydispersity, melt index, etc.) been build up along the reactor height and also to predict the polymer particle growth. The guidelines followed by Zabisky et al (1992) were adapted to the case of the coordination copolymerization reaction mechanism outlined by McAuley et al (1990) and to the dynamics along the reactor height. The model consisted of 36 differential equations corresponding to the components material balances and the life and dead polymers moments, plus accessories equations to account for calculation of polydispersity, density, comonomer incorporation in the polymer chain and others calculated characteristics.

To connect the results from the reactor model (temperature, concentration and production profiles obtained in function of the height position) with the results from the method of moments' predictions (concentration, production and quality profiles obtained in function of the time) an iterative process was created. Outputs from the reactor model served as inputs for the physical-chemical model, and vice-versa, so that adjustments on operational parameters could be done in both models, till the profiles obtained from both models matched in terms of ethylene and comonomers concentrations and production of polyethylene. The difficulty of this operation had relied on the different integration variables (time and position) of the two models, what complicates the convergence of the system to a single matching result.

## RESULTS

The data that have been obtained with the reactor model have shown interesting results concerning to the temperature and concentration gradients in the reactor, specially at the catalyst feeding region, where the reaction rate is greater due to the higher temperature and to the higher influence of the catalyst in the formation and early development of young polymer particles. The case illustrated by figure 1 shows a typical temperature and concentration gradient profiles given for the production of polyethylene in a fluidized bed reactor with no prepolymerization. The data used in the models simulations are shown in table 2.

As it can be observed from figure 1, the top portion of the reactor requires special attention in order to not present hot spots or even the melting of the polymer. According to the parametric study of the system, this situation can be avoided by controlling the gas feed velocity and temperature. In terms of polyethylene production, it can be enhanced by elevating the gas feed temperature, and by decreasing the gas feed velocity. It was observed that an increase of 15K in the gas feed temperature can multiply the production of polyethylene by up to 50% (not shown), without compromising the polyethylene characteristic and integrity.

The physical-chemical model, alone, shows that the average molecular weight of the polymer increases more intensely at the beginning of the polymerization period and slows down after a while. The polydispersity follows the same increase profile. Density and comonomer incorporation on the polymer remains practically constant during the entire polymerization process (not shown).

The figure 2 shows the simulation of the polyethylene physical-chemical characteristics build up inside the fluidized bed reactor, obtained by the link of the reactor and the physical-chemical characterization models. The simulation shows that there is a highly active reaction zone in the top of the reactor, what is in accordance to the reactor model. Beneath this highly active zone, follows a less active zone responsible for the refining of the polymer characteristics.

The upper and highly reaction active zone tends to be less evident when prepolymerization of the polyethylene particles are employed (not shown).

The assumption that the polymer particles segregates inside the reactor still holds up, with fine particles being at the reactors' top and heavier particles being distributed along the reactor height.

## CONCLUSION

In this work a new reactor and physical-chemical characterization models were developed and linked together to give a complete understanding of the fluidized bed reactor for polyethylene production.

The reactor model developed permits the usage of a more complex reaction mechanism and the prediction of the polymer average particle diameter and polymer/catalyst weight fraction. But more than all, it also extends the possibility of simulation of the reactor operating with low degree or no prepolymerization, case which the models based on the well-mixed emulsion phase theory are incapable to predict correctly.

The two models when linked together become very useful tool to perform a complete optimization of the fluidized bed reactor for the production of polyethylene, since it makes possible to optimize the reactor conditions looking for an enhancement on the polyethylene production rate and at the same time check how the changes on the operational conditions of the reactor influence on the grade of polymer being produced.

From the industrial point of view, these more reliable copolymerization models are capable of simulating the synthesis conditions of the polyethylene and permit the study of new copolymers previously to industrial tests. In this way, new polymer grades can be developed more easily, and existents grades can be optimized in order to produce high quality resins.

## NOTATION

|            |   |
|------------|---|
| A          | sectional area of the reactor                       |
| $C_{ij}$   | concentration of the component $j$ in the $i$ phase |
| $C_{p,gj}$ | molar heat capacity of the gas component $j$        |
| $C_{p,s}$  | mass heat capacity of the solids                    |

|                 |  |
|-----------------|--|
| D               | fluidized bed reactor diameter                                   |
| $\Delta H$      | heat of reaction   |
| $H^*$           | molecular hydrogen   |
| $H_m$           | heat transfer coefficient  |
| $K_{mj}$        | mass transfer coefficient of the component $j$                   |
| $M_w$           | ethylene molecular weight  |
| NC              | number of components   |
| $P(r)$          | non-reactive polymer with chain length size $r$                  |
| $q_{cat}$       | catalyst feeding rate  |
| $R^*$           | potential active site  |
| $R_i(r)$        | live polymer with terminal monomer $i$ and chain length size $r$ |
| $R_p'$          | polyethylene production rate                                     |
| $T_i$           | temperature of the $i$ phase                                     |
| $T_{ref}$       | reference temperature  |
| $U_i$           | velocity of the $i$ phase  |
| $U_h$           | wall heat transfer coefficient                                   |
| X               | cocatalyst   |
| z               | height above the distributor                                     |
| $\delta$        | bubble volumetric fraction in bed                                |
| $\epsilon_{mf}$ | minimum fluidized porosity                                       |
| $\chi$          | catalyst/polymer average weight fraction                         |

#### subscripts

|    |                               |
|----|-------------------------------|
| 1  | ethylene                      |
| 2  | 1-butene                      |
| b  | bubble phase                  |
| e  | emulsion phase                |
| mf | minimum fluidizing condition  |
| T  | total (sum of all components) |

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#### TABLES AND FIGURES

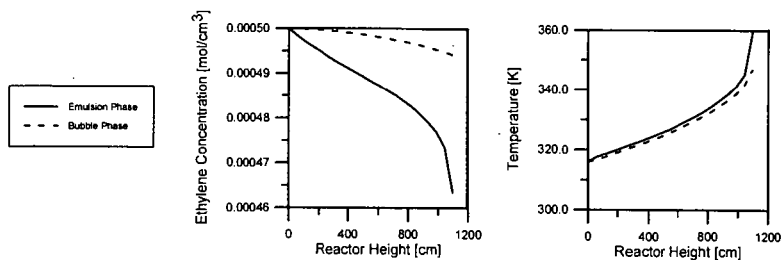
Table 1. Reaction Mechanism and Kinetic Parameters

| Reaction                              |   |                  | Catalytic Site 1 | Catalytic Site 2 |
|---------------------------------------|---|------------------|------------------|------------------|
| formation [ $s^{-1}$ ]                | $R^* \xrightarrow{k_f} R_0$                 | kf               | 1                | 1                |
| initiation<br>[ $L.mol^{-1}.s^{-1}$ ] | $R_0 + C_i \xrightarrow{ki} R_i(I)$         | ki <sub>1</sub>  | 1                | 1                |
|                                       | $H^* + C_i \xrightarrow{khi} R_i(I)$        | ki <sub>2</sub>  | 0.14             | 0.14             |
|                                       |   | kh <sub>1</sub>  | 1                | 1                |
|                                       | $H^* + X \xrightarrow{khr} R_X(I)$          | kh <sub>2</sub>  | 0.1              | 0.1              |
| propagation                           |   | kh <sub>r</sub>  | 20               | 20               |
|                                       | $R_i(r) + C_k \xrightarrow{kpi k} R_k(r+1)$ | kp <sub>11</sub> | 85               | 85               |

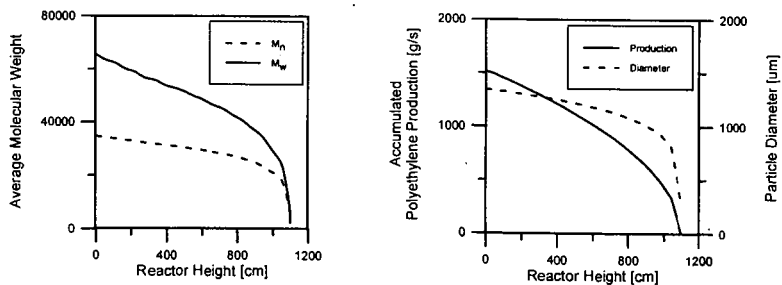
|   |  |                  |        |        |
|---|--|------------------|--------|--------|
| [L.mol <sup>-1</sup> .s <sup>-1</sup> ] |  | kp <sub>12</sub> | 2      | 15     |
|   |  | kp <sub>21</sub> | 64     | 64     |
|   |  | kp <sub>22</sub> | 1.5    | 6.2    |
| chain transfer                          | $R_i(r) + C_k \xrightarrow{kfmik} P(r) + R_k(l)$ | kf <sub>11</sub> | 0.0021 | 0.0021 |
| [L.mol <sup>-1</sup> .s <sup>-1</sup> ] |  | kf <sub>12</sub> | 0.006  | 0.11   |
|   |  | kf <sub>21</sub> | 0.0021 | 0.001  |
|   |  | kf <sub>22</sub> | 0.006  | 0.11   |
|   | $R_i(r) + H_2 \xrightarrow{kfh1} P(r) + H^*$     | kfh <sub>1</sub> | 0.088  | 0.37   |
|   |  | kfh <sub>2</sub> | 0.088  | 0.37   |
|   | $R_i(r) + X \xrightarrow{kfr1} R_X(l) + P(r)$    | kfr <sub>1</sub> | 0.024  | 0.12   |
|   |  | kfr <sub>2</sub> | 0.048  | 0.24   |
|   | $R_i(r) \xrightarrow{kfs1} P(r) + H^*$           | kfs <sub>1</sub> | 0.0001 | 0.0001 |
|   |  | kfs <sub>2</sub> | 0.0001 | 0.0001 |
| deactivation [s <sup>-1</sup> ]         | $R_i(r) \xrightarrow{kds} P(r) + R_D$            | kds              | 0.0001 | 0.0001 |

**Table 2.** Operational conditions and reactor data used in the simulations

|                      |                        |                      |            |
|----------------------|------------------------|----------------------|------------|
| Ethylene feed rate   | 0.50 mol/L             | 1-Butene feed rate   | 0.20 mol/L |
| Hydrogen feed rate   | 0.05 mol/L             | Inert feed rate      | 0.00 mol/L |
| Catalyst feed rate   | 0.20 g/s               | Cocatalyst feed rate | 0.01 mol/L |
| Gas feed temperature | 316 K                  | Room temperature     | 340 K      |
| Catalyst density     | 2.38 g/cm <sup>3</sup> | Catalyst diameter    | 0.05 mm    |
| Activation energy    | 37620 J/mol            | ΔH                   | -3829 J/g  |
| Reactor diameter     | 396 cm                 | Reactor height       | 1097 cm    |
| δ                    | 0.214                  | ε <sub>mf</sub>      | 0.50       |
| U <sub>mf</sub>      | 7.0 cm/s               | U <sub>c</sub>       | 34.8 cm/s  |
| U <sub>b</sub>       | 114.0 cm/s             | Bubble diameter      | 15 cm      |



**Figure 1.** Ethylene concentration and temperature gradients for the production of polyethylene in a fluidized bed reactor with no prepolymerization. Simulation data from table 2.



**Figure 2.** Average molecular weight ( $M_n$  and  $M_w$ ), accumulated polyethylene production and particle diameter build up profiles inside the fluidized bed reactor. Simulation data from table 2.